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The Response of Explosives to Accidental Stimuli

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Preface

This brief discussion of the non-shock response of explosives is intended to introduce the reader to the basic concepts involved, and as additional reading to a live class on the subject.

Introduction

Explosives are generally designed to detonate – a specific kind of explosion in which a shock wave – a supersonic discontinuity in pressure, density and particle velocity – passes through the material and triggers fast chemical decomposition, liberating energy that is available to support the shock wave which would otherwise die out. The result may perhaps be usefully visualized as a rocket-propelled shock wave.

Ideally, an explosive would detonate reliably when required while behaving as an inert material in all other circumstances. Modern engineered explosives, such as those used in nuclear weapons, largely meet the first criterion but fail the second because, even though they are very difficult to detonate unintentionally, they also exhibit non-detonative energetic decomposition responses to accidental stimuli that can range from mild to very violent.

There are two distinct elements to a full understanding of this regime of behavior:

1. How do accidental stimuli cause the onset of decomposition?
2. What determines the violence of the ensuing reaction?

In order to understand these elements we must first consider the full range of behaviors of commonly used explosives. This course is intended to introduce the student to the basic concepts and to encourage further reading on the subject.

Classes of Explosives

Secondary Explosives

Most of the explosives that we deal with are referred to as *secondary* explosives. For simplicity we will include what are sometimes called *tertiary* explosives in this category, since they exhibit the same fundamental behaviors. In these materials (with a few exceptions discussed later), a detonation wave will not form spontaneously and a shock wave must be supplied as an external stimulus in order for detonation to occur¹. We will refer to this process of starting a detonation as *initiation*, and the strength of shock required to achieve this as the explosive's *shock sensitivity*.

Note the potential for confusion here, since a shock-sensitive explosive has a low shock sensitivity (threshold shock pressure) value.

Secondary explosives may, however, also undergo a form of energetic decomposition known as *deflagration* – a process that follows an ignition (thermal, mechanical, electrical etc.) stimulus. Depending on the explosive, its form (loose powder, pressed, plastic-bonded etc.), confinement and quantity, a deflagration can range from a relatively slow process that looks like a simple burn to a fast, violent explosion that, at a distance, is almost indistinguishable from detonation but lacks the shock wave.

This illustrates a significant point – that while the failure of an explosive to detonate in the absence of an initiating shock wave is important from the perspective of weapon surety, a violent explosive reaction is almost as destructive as a detonation to nearby personnel, and in that sense it makes little difference from the safety point of view.

Secondary explosives vary from very insensitive to moderately sensitive, with loose powders and large pressed charges generally representing the greatest hazards, for reasons discussed below.

Primary Explosives

Primary explosives differ from secondary explosives in that they do not undergo deflagration. Ignition, either by thermal or mechanical stimulus, leads to almost immediate detonation, making them suitable as the first element in an initiation train.

Despite the standard classification of primary explosives based on sensitivity to ignition, note that the defining characteristic of a primary explosive is actually this ability to detonate without a shock stimulus^{1,2}. As an example, most of the metal salt primary explosives, such as lead azide, are significantly more thermally stable (higher decomposition temperatures) than most secondary explosives, even though their commonest form of ignition is direct heating. Primary explosives are more impact and shock sensitive however, a property that is related to their ability to transition rapidly to detonation.

Propellants

Propellants are a class of energetic materials that are designed to deflagrate in order to provide propulsion in the form of hot, high-pressure, gaseous decomposition products³. Gun and rocket propellants are common examples. While they are not intended to detonate, some are capable of detonation if misused, and all are capable of violent reaction if ignited with confinement. Propellants are often more sensitive to stimuli, especially impact and static electricity, than many of the engineered high explosives that we deal with, and should be handled accordingly.

Design-Mode Initiation

In the design mode operation of secondary explosives, the required initiating shock is supplied by a detonator, a device that generally functions by one of two basic processes:

Primary-Based Detonators

A detonator may contain a primary explosive that is initiated by a thermal (or sometimes mechanical) stimulus leading directly to detonation. The initiation is usually a low-voltage bridgewire (non-exploding) or a nonel (non-electric) lead line.

These are often referred to as *low-energy* detonators, although once again this is somewhat misleading since they are more accurately defined by their ability to detonate at low input power levels – mostly represented by low voltages and bridgewire currents. Since they contain primary explosives they have only one response to ignition – detonation.

Low-voltage detonators are deprecated at LANL, primarily due to the possibility of stray radio-frequency emissions inducing sufficient current in the bridgewire to initiate the device. The nonel versions of these detonators, however, are far less susceptible to accidental initiation, and are commonly used where the precise timing that is provided by high-voltage detonators is not required.

Non-Primary-Based Detonators

A detonator may lack any primary explosive but instead include a feature, such as a high-voltage exploding bridgewire or an electrically or laser-driven foil flyer, that is capable of putting a strong enough shock wave directly into a shock-sensitive secondary explosive to cause detonation.

These are often referred to as *high-energy* detonators, but are better described as *high-power* or *high-voltage* detonators. The exploding bridgewires or foils typically require 2 – 5 kV discharges from 1 μ F capacitors in order to function properly. Lower power stimuli may ignite the secondary explosive in these detonators and they may even explode, but will not detonate and so will not initiate the main charge, making them safer to use than primary-based detonators.

This class of detonators includes exploding bridgewire (EBW) and exploding foil (EFI – also known as slappers). These devices are the most commonly used at LANL, and are found in most weapon applications and testing.

Non-shock Response

With the exception of primaries, most explosives are far too insensitive to shock initiation for this to be a credible handling hazard. For example, impact speeds of several hundreds of meters per second are required to generate strong enough shock waves – unattainable in most situations.

Having ruled out accidental shock initiation of detonation as a likely handling hazard, we instead consider the non-shock mechanisms by which ignition, leading potentially to propagation of a deflagration, may occur.

The observation that ignition and propagation are two quite distinct and decoupled processes suggests another important point. Safety is maximized if we avoid accidental ignition altogether, but a comprehensive hazard analysis takes into account severity of consequence – in this case

violence of reaction propagation – as well as probability of occurrence. The probability of an accident is determined by the ignition process but the consequence is determined by propagation, and so we must consider both.

Thermal Effects on Explosives

Fundamentally, all ignition processes are thermal⁴. Even if the original stimulus is mechanical, such as an impact, ignition occurs by potential or kinetic energy being degraded to heat and causing the temperature of the explosive to rise locally above its ignition temperature. Accordingly, we consider first the response of explosives to increased temperature.

Explosive Thermochemistry

At ambient temperatures we regard explosives as physically and chemically stable – effectively correct on timescales of interest. As the temperature rises, various physical and chemical changes may occur; thermal expansion may lead to deformation or cracking, explosive or additives may melt or undergo other phase changes, and chemical decomposition may begin. While physical changes may have a significant effect on propagation of reaction (should ignition occur), at this stage we are primarily interested in the chemistry.

The decomposition chemistry of explosives is generally very complex, with tens, if not hundreds, of reactions associated with the formation of reaction intermediates and final products. We typically simplify this problem by reducing the initial solid-state (pre-ignition) reactions to a few (or sometimes just one) representative steps that effectively describe the rate of reaction and energy release as a function of temperature and extent of reaction. When this is done we find that most explosives exhibit a reaction rate that, above a certain onset temperature, increases exponentially with temperature up to ignition – which we define as the start of the fast, pressure- and temperature-dependent gas-phase reactions that liberate most of the energy of combustion.

This is a very significant aspect of the behavior of explosives, and accounts both for the observed rapid thermal runaway once an explosive gets hot enough and for the very high reaction rates at high temperatures. It also explains the observation that time to ignition is a strong function of temperature. For example, at 220°C HMX will ignite in a few tens of seconds, while at 600°C it takes less than a millisecond⁵.

When an explosive sample is heated, the temperature rise is initially determined by the externally supplied heat but, above a certain critical temperature, heat produced by exothermic decomposition is sufficient to continue heating the remaining material even if the external heat source is removed – a very significant hazard. This process will result in thermal cookoff of the sample and, depending on the sample size and confinement, may produce anything from a low-pressure deflagration to a very violent explosion.

Bulk Thermal Heating

While an idealized view of heating explosives, bulk thermal heating is not an entirely unrealistic scenario since it is approximately what occurs when an explosive is heated slowly in an oven or by some other spatially extended heating source⁶.

The key feature of bulk heating is that we supply enough heat over a sufficiently large volume that there is no question whether the explosive actually gets hot. We are implicitly ignoring the time-dependent process of thermal transport and assuming that all the explosive is at roughly the same temperature during the heating process (the classical Semenov well-mixed reactor thermal explosion model) – i.e. it is not being kept cool by thermal transport away from a finite-size hot zone. This is a reasonable assumption, at least until the onset of exothermic reaction and self-heating begins to predominate.

Bulk thermal heating of explosives is commonly used in drying, casting, pressing and conditioning, and represents a very common hazard. Knowledge of the thermal response allows us to develop controls to prevent explosives from being heated beyond safe temperatures.

Localized Thermal Heating

When an explosive is heated in a small local region, such as typically occurs in impact or friction events, the chemistry is the same but we can no longer ignore the effect of thermal transport that allows heat to be conducted away from the hot zone⁷. This is additionally important because this kind of heating is often transient in nature.

Let us assume that a quantity of heat is quickly deposited in a small volume of explosive, raising its temperature high enough that significant exothermic decomposition starts to take place. We now observe a competition between generation of heat by the exothermic reaction and loss of heat by conduction into the surrounding cooler material (the classical Frank-Kamenetskii hot-spot model).

Since the heat generation rate (reaction rate) is temperature dependent and the rate of cooling by thermal conduction is temperature-gradient dependent, we find that there exists a certain critical hot-spot size (for a given hot-spot temperature) or a critical hot-spot temperature (for a given hot-spot size) above which the hot spot will grow and the temperature will increase until ignition occurs. This critical hot-spot size/temperature thus plays a pivotal role in determining the outcome of a transient, localized heating event.

Localized heating is never performed intentionally, and when handling explosives we attempt to prevent any mechanisms that may cause this to happen. In common handling scenarios, the major hazard of this type is from frictional interactions, which we discuss further below.

Non-thermal heating processes

We next consider heating mechanisms other than the direct application of heat. Fundamentally there are only a few, but they may arise in a number of distinct ways and often appear different even if they are not.

Mechanical Deformation

The commonest class of insult to explosives is some kind of mechanical deformation⁸, whether by impact, crushing, pinching or penetration, but the mechanisms by which an explosive is heated to ignition by these events are often misunderstood.

Explosives, in common with most solids, exhibit elastic-plastic behavior. By this we mean that when stress is applied they first deform elastically up to a certain strain, and beyond that deform plastically until they break (failure).

In the initial elastic regime, the work done is stored in the manner of a spring and released when the applied stress is removed. There is no permanent deformation and the work is not degraded to heat so there is no temperature rise. However, most solid explosives have only a very limited elastic response (very low elastic limit) and so we mostly neglect this regime.

In the plastic regime the explosive is permanently deformed and the work done is not stored but instead degraded to heat (a dissipative process), increasing the temperature of the material. However, explosives are rather weak solids, with plastic deformation and failure occurring (at least at low strain rates) at low stresses. A consequence of this is that relatively little work is actually done in the process, and the associated temperature rise is quite small – too small, in general, to cause ignition. We again exclude primary explosives from the discussion, since their higher strength (from partially ionic bonding) and mechanical sensitivity does present a significant hazard.

The key concept is strain rate – the rate of deformation of the material – and it turns out to be neither simple nor intuitive in many situations. The reason that it is important is that, at higher strain rates, other dissipative processes beyond simple plastic deformation may be activated and are capable of depositing heat at much higher rates. Of particular relevance here are conditions of high pressure and shear that can lead to a process called *visco-plastic flow*, in which the material flows like a viscous liquid and significant work is done by the viscous forces.

These are precisely the conditions that obtain in a drop-weight test, in which the highly parallel anvils constrain the explosive to undergo very high-velocity and high-pressure radial flow, leading to intense visco-plastic heating as the anvils come together.

This effect explains why one may observe ignition of PBX 9501, for example, in a drop-weight test at impact speeds of a few meters per second, while getting no reaction at all with a projectile impact on a bare charge of the same material at 150 ms^{-1} . In the latter case, even though the impact velocity is much higher, the deformation region around the projectile is less constrained and much larger, leading to lower maximum strain rates and insufficient visco-plastic heating.

A further example of pressure/shear ignition is seen in the Steven test, in which a blunt-nosed projectile impacts covered disk of explosive with a relatively massive steel back plate. The test is notable (and popular) because it exhibits a surprisingly sharp transition from *no-go* to *go* as impact speed is increased. However, rather than probing a continuous regime of explosive response to impact (its original intent), it turns out to be a simple measurement of how fast the projectile has to hit to pinch the explosive against the back plate and produce radial flow similar to a drop-weight test.

To our advantage is that these rather extreme conditions are very difficult to achieve in normal handling operations, and so, the fundamental conclusion with regard to mechanical insults is that for secondary explosives, unless the event somehow accesses the high-pressure, high-shear regime, ignition is unlikely, at least due to pure mechanical deformation. Simply dropping a

charge, even a large one, will not lead to ignition by deformation or fracture, but there is a significant caveat that other processes, especially frictional effects (discussed next), may also occur as charge size increases and may lead to ignition.

Frictional Heating

Frictional processes involving explosives are perhaps the most dangerous and misunderstood of all heating mechanisms⁹.

With the exception of primary explosives, it turns out that direct frictional heating of explosives almost never causes ignition. The reason is simple. In addition to the weakness of the material, mentioned previously, that again limits the rate of deposition of heat, a universal characteristic of frictional interactions between two solids is that the maximum temperature achievable is limited to the melting point of the lower-melting-point solid involved. Almost all the explosives that we use melt at temperatures either below or around the temperatures at which significant thermal decomposition occurs.

Since heating only occurs at the interface (localized heating), thermal transport away from the surface cools the heated explosive – i.e. the Frank-Kamenetskii hot-spot model applies. Even if the frictional interaction is sustained it is difficult to get the temperature high enough to cause ignition, but in most scenarios, such as dropping on a rough surface, the frictional heating of the explosive is transient and the temperatures achieved are well below those needed for ignition on the timescale of the event. Rubbing an explosive against a surface, however rough and whatever its melting point, is not a likely ignition mechanism.

But, we know that frictional interactions are a significant cause of ignition, so what are we missing? The answer is the involvement of other high-melting-point solids, and the commonest culprit is grit.

If an explosive charge is dropped on a high-melting-point surface with grit present, the grit particles are likely to become embedded in the explosive and dragged across the other surface. Now we have two high-melting point solids (the grit and the surface) interacting, and the grit can get very hot, very fast. Taking sand and a glass surface, for example, the sand particles can reach hundreds of degrees Celsius in around 100 μ s, and, since they are embedded in the explosive, form a critical hot spot that will ignite within the typical 1 ms duration of the impact event.

While this ignition may or may not lead to propagation of a bulk deflagration, it potentially only takes one grit particle to start the reaction.

An understanding of this process immediately suggests the principle measure that we take to mitigate the hazard – the use of low-melting-point surfaces wherever we handle charges large enough to present a risk from this mechanism. If the surface has a low melting point, then even if grit is present there is nothing for it to interact with to generate high temperatures.

Dropping large, consolidated charges produces the greatest risk from frictional effects, since the mass of the charge both increases the interaction forces on impact, leading to a higher probability of significant heating of trapped grit, and provides a larger charge in which the ensuing reaction has a chance to build to a violent reaction.

Other Notable Heating Mechanisms

A few other heating mechanisms deserve specific mention, due either to the level of hazard they present or the singular nature of the threat.

Cased Explosives

Explosive charges are often cased with metal. Recall from the discussion of mechanical deformation that the temperature rise in explosives is limited by their low mechanical strength. Metals, however, are much stronger, and the fracture energy liberated when they are deformed can be sufficient to produce a much larger temperature rise.

A particularly hazardous situation arises when the metal casing of an explosive is penetrated by a projectile, even if the impact speed is too low for shock initiation. If a fragment of casing is punched out by the impact and lodged in the explosive, then the fractured surface of that fragment may easily be hot enough to lead to a critical hot spot and ignition of the charge.

Other hazards arise if metal tools are used on cased explosive, introducing the possibility that interaction of the tool with the casing may lead to high temperatures, or possibly sparking.

Screw Threads

If small amounts of explosive contaminate screw threads, the high pressure and shearing conditions may be sufficient to cause ignition. Under the high confinement the reaction may be violent enough to eject the bolt and/or the hot products may thermally ignite the bulk explosive in the assembly.

Explosives Machining

Most machining operations are surface processes, involving removal of small thicknesses of material on each pass and, as such, generate only small temperature rises that are readily cooled by conduction.

Drilling is the exception, and presents two additional hazards. Firstly, the cutting process is inside the bulk material and more difficult to cool. Over an extended period the explosive may get hot enough to begin to self-heat. Secondly, and especially with small-diameter, deep holes, there is the risk that the drill bit snaps and the two broken surfaces rub against each other, leading to significant frictional heating and a potential critical hot spot within the explosive.

Machining of explosives (with just a few exceptions) is performed remotely, at slow speed, and with liquid cooling of the tools and explosive.

Electrostatic Discharge

Most secondary explosives are insensitive to electrostatic discharge at the level possible from human capacitance, although powders, especially fine powders, are more susceptible to ignition¹⁰.

As a result, workers always wear grounding straps or stand on conductive flooring when working with static-sensitive materials.

Sensitivity Tests

A standard suite of sensitivity tests, including impact, spark, friction, vacuum stability at elevated temperature, and onset temperature of decomposition, are commonly used to assess explosives¹¹. The results are a useful guide to relative sensitivity, but not an exhaustive assessment of potential hazards.

Explosives that appear to be more sensitive than PETN are generally labeled and handled as primary explosives (1.1A), although this is more of an administrative control than an accurate description.

Propagation of Reaction – the Question of Violence

The discussion above focused almost entirely on ignition, and clearly, if we can avoid accidental ignition then we will achieve our safety goals. However, as stated earlier, a full hazard analysis includes severity of consequence, and our acceptance of risk (sometimes unavoidable) is generally influenced strongly by consequence. For example, the risk of an ignition event that will not lead to anything more than mild deflagration of a small sample of explosive is much more acceptable than one that may produce the violent explosion of a large charge.

While the propagation of deflagration is often much harder to predict than ignition, since it depends strongly on many more, and less well characterized, properties of the explosive¹², we can still draw a number of empirical conclusions about potential outcomes.

Reaction Rates and the Effects of Pressure and Confinement

As mentioned previously, pre-ignition, solid-state reaction rates are highly temperature dependent but only slightly pressure dependent. Once ignition occurs and the explosive begins to undergo the much faster and more energetic, surface-regressive, gas-phase reactions that characterize deflagration, reaction temperatures are largely fixed by the thermochemistry of the reactions, while pressure and accessible surface area become the dominant intensive* factors in determining reaction rate.

In general, the reaction rate, \mathcal{R} , of a deflagration is linearly dependent on accessible surface area, A , and dependent on pressure, p , to the power n , where n is typically around 1:

$$\mathcal{R} = Ap^n$$

An important implication of this relationship is that confinement has a very significant effect, since it contains the product gases and causes the pressure to rise, increasing the reaction rate further.

A further, equally important but less obvious, effect is that as the pressure increases the accessible surface area may also increase. The minimum size of crack or void that a gas-phase reaction (flame) can occur in is pressure-dependent, since increasing the pressure decreases the

* Mass- or size-independent

flame standoff from the burning surface. This is the same effect that is responsible for the rate dependence on pressure by increasing the rate of energy feedback to the surface, but here it also allows the flames to penetrate smaller and smaller features.

The sensitivity to confinement is well illustrated by the demonstration that a small, unconfined pile of black powder will burn fast, but smoothly, when ignited. Placing that same material in just a thin paper bag leads to a noticeably more explosive reaction, and putting it in a coffee tin leads to a violent explosion.

For some of the types of explosive that we commonly use, such as PBX 9501, it is worth observing that even a large charge, if pristine and unconfined, when ignited on the surface will burn steadily since the pressure does not increase. If, however, confinement is applied and if the charge is damaged, flame intrusion into the bulk as the pressure increases can lead to very violent reaction.

Confinement need not be supplied by an external container – just the inertial mass of an explosive charge provides confinement if the reaction occurs in the interior – and so it is also generally true that, all other things being equal and for an interior ignition, the risk of violent reaction increases with charge size. As an extreme example, even a material that is barely an explosive, such as ammonium nitrate, can, in sufficiently large quantities (hundreds of tons) undergo extremely violent reaction if it gets hot enough.

Deflagration-to-Detonation Transition (DDT)

Although, as mentioned earlier, even a fast, violent deflagration can be nearly as destructive as a detonation, we are still concerned with other collateral effects of detonation, and especially the possibility of causing sympathetic detonation in other nearby charges, leading to a much larger overall event.

There are processes by which a shock wave, necessary for detonation, can arise from a non-shock deflagration of an explosive¹³. These are more likely to occur in more shock sensitive explosives, thermally or mechanically damaged charges, loose powder, large charges, and heavily confined charges. It is also more likely to occur as a result of cookoff than from ignition at ambient temperature.

While this is not the place for a detailed discussion of DDT mechanisms, the process often proceeds through a sequence of ignition, laminar deflagration (smooth surface regression), convective burning (flame intrusion into cracks and voids), compressive burning (strong compressive waves causing ignition by mechanical deformation ahead of the deflagration wave), and, ultimately, shock formation. Associated with each of those stages is a significant increase in both pressure and the time-derivate of pressure, and so inertial effects can supplement the physical confinement of the system.

Summary

Even in the absence of design-mode initiation, explosives are capable of undergoing ignition and deflagration that may be extremely violent. The factors that determine such behaviors are neither

simple nor intuitive in many cases, and a mechanistic understanding of the basic principles is an important tool in the safe use and handling of explosives.

In addition, it should be stressed that, especially with new or unusual explosives, unanticipated mechanisms may exist and that continual and vigilant reassessment of all procedures involving explosives is essential.

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